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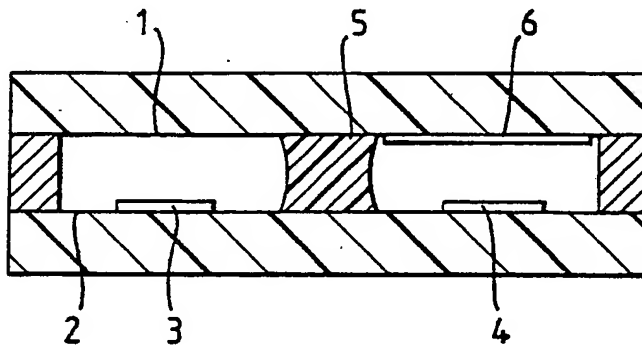


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(54) Title: TEST DEVICES WITH REAGENT LAYERS FORMED BY PRINTING PROCESSES



## (57) Abstract

A test device for carrying out a microchemical test, comprises a container for contacting a reaction liquid during performance of said test, said container having deposited on a surface thereof which in use is to contact said reaction liquid, an adherent layer applied in an amount in the range 1 to 40 mg/sq cm comprising a chemically or electrochemically active material which has been deposited in the form of a composition comprising solid particles having a particle size in the range 0.5 to 25, e.g. 1 to 20, microns, together with a polymeric binder. A corresponding printable composition for printing a layer of a chemically or electrochemically active material on to a surface of a substrate to form such a device comprises (a) a chemically or electrochemically active substance to be deposited, dissolved in (b) a (e.g. aqueous) solvent for said substance (a), (c) a polymeric binder or thickener dissolved or dispersed in solvent (b), (c) from 1 to 15 percent by weight of a dispersed finely-divided inert particulate material with a particle size in the range 1 to 50 microns, and has a viscosity in the range 1 to 250 poise at 25 deg.C.

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Test devices with reagent layers formed by printing processes.

5 This invention relates materials for microchemical testing, and to their preparation and use, and especially to test devices containing reagent layers which have been formed by printing processes. Thus the invention relates especially for example to processes for printing materials which are to form functional or reactive portions of devices such as carriers of chemical reagents or electrical and electrochemical devices and components. 10 The invention also relates to certain printable compositions which can be used in such processes and the devices produced by the processes.

15 Screen-printing and contact printing are well known in themselves, as are many compositions of ink and coatings to be applied by their use. It is also common for printing inks to contain particulate material, e.g. as in EP 0 202 656 (Canon KK).

20 EP 0 171 148 and 0 170 375 (Unilever) describe the construction of capillary-fill devices, including the deposition of adhesive patches containing solid particulate or fibrous material to regulate the spacing 25 apart of opposite walls of the devices.

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EP 0 188 232 (Nippon Paint KK) discloses radiation-curable liquid resin compositions incorporating 0.01-6 micron polymer microparticles, and also mentions a use of such materials for immobilising enzymes.

GB 2 040 946 (STC) discloses inks for screen printing electrical components, based on phenol resins, and loaded with silver flake or powdered silica.

Also included in the prior art are a number of enzyme electrode measurement methods, in one of which an enzyme (urease) is chemically bound to a ptfe membrane which is an integral part of an ammonia gas membrane electrode incorporating an ammonia permeable membrane, (e.g. M Mascini and C G Guilbault, Anal Chem. 49 (6) 1977, pp 795-798).

Also known are electrochemical cells mounted within capillary-fill devices, as described in European Patent Application No. 0 170 135 (Unilever).

We have encountered difficulties in the formulation of materials which are to be printed in a pattern-wise manner and which are to have chemical reactivity or defined chemical or electrochemical properties. This invention aims to solve certain such difficulties.

Thus, an aim of the invention is to provide conveniently printable compositions for the placing of small active areas of layers of desired reagents in chemical test devices, e.g. for immunological and/or electrochemical testing. The details of such tests in themselves are not however the subject of the present invention, and reference is made to the prior art for such details.

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The present invention also provides useful processes for coating reactive materials on to or to form such electrodes, or on to or to form composite test devices embodying electrodes, and relates also to the  
5 corresponding compositions, electrodes and devices so formed.

According to one aspect of the present invention, we provide a process for printing a chemically or  
10 electrochemically active material on to a surface, wherein said material is a flowable material, and wherein suspensible hydrophobic or hydrophilic particles are incorporated into the material before printing.

15 By the invention there is also provided a test device for carrying out a microchemical test, comprising a container for contacting a reaction liquid during performance of said test, said container having deposited on a surface thereof which in use is to contact said  
20 reaction liquid, an adherent layer applied in an amount in the range 1 to 40 mg/sq cm comprising a chemically or electrochemically active material which has been deposited in the form of a composition comprising solid particles having a particle size in the range 0.5 to 25,  
25 e.g. 1 to 20, microns, together with a polymeric binder.

The particles can comprise inert particles, e.g. ptfe or silica gel, and can be dispersed in a matrix comprising said active material and a polymeric binder,  
30 e.g. a water-soluble cellulose derivative. Alternatively, said active material can be used in solid finely-divided form, and dispersed in such a polymeric binder.

35 A process according to the invention, for manufacturing such a test device, comprises printing a

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layer of a chemically or electrochemically active material on to a surface of a substrate which is to form an inner surface of a container for carrying out a microchemical test, said process also comprising: (a) providing a printable composition comprising said chemically or electrochemically active material, together with suspensible hydrophobic or hydrophilic particles having a particle size in the range 0.5 to 25 microns, (b) printing said printable composition containing said particles on to said substrate to form a layer on said surface, and (c) causing said layer to dry or solidify.

In the process, said chemically or electrochemically active material can be water-soluble, e.g. selected from enzymes, antigens, antibodies, electron transfer agents able to react with enzymes, or pH buffer materials. Alternatively, the active material may be water-insoluble, e.g. an ion-selective ionophore material.

Particle size can usefully be in the range from at least about 3 micron to at least about 15 micron, and the particles can be selected from ptfе, silica-gel, polystyrene, polymer latex, and comminuted solids comprising the chemically or electrochemically active material to be deposited. The particles can be used in an amount from at least about 1 percent to at least about 60 percent, e.g. about 5 to about 15 percent, by weight of the printable composition.

The invention correspondingly provides a printable composition for printing a layer of a chemically or electrochemically active material on to a surface of a substrate to form a device as described herein, comprising (a) a chemically or electrochemically active substance to be deposited, dissolved in (b) a (e.g.

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aqueous) solvent for said substance (a), (c) a polymeric binder or thickener dissolved or dispersed in solvent (b), (c) from 1 to 15 percent by weight of a dispersed finely-divided inert particulate material with a particle size in the range 1 to 50 microns, said composition having a viscosity in the range 1 to 250 poise at 25 deg.C.

An alternative form of printable composition comprises (a) a polymeric binder or thickener dissolved or dispersed in a (e.g. nonaqueous) solvent, having dispersed therein (b) from 5 to 60 percent by weight of a chemically or electrochemically active (e.g. water-soluble or water-dispersible) substance to be deposited, in finely-divided solid particulate form having a particle size less than 20 micron, preferably less than 10 micron, said composition having a viscosity in the range 1 to 250 poise, preferably at least about 150 poise, at 25 deg.C.

The printable composition can usefully show shear-thinning of at least about 0.1 log viscosity per tenfold increase of shear rate in the range of shear rates about 10 to 100 reciprocal seconds, and has a viscosity at 200 reciprocal seconds at 25 deg.C. in the range 1 to 35 poise.

The preferred printing techniques for use in this invention are screen-printing and variants thereof including contact printing e.g. using stencils. Layers of printable composition can be laid down at thicknesses ranging up to about 400 micron, and give dried layers at up to about 40 mg/sq cm, but it is often preferred to work at about a tenth of these levels, e.g. in the range of at least about 1 to at least about 10 mg/sq cm.



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The particles can for example be about 0.05 micron to 25 micron in size, e.g. above about 0.5 micron, especially about 3 to 15 micron. We have found that the incorporation of such particles can usefully increase viscosity at low shear, and/or impart or enhance shear-thinning properties in the materials to be printed, and/or reduce extensional viscosity of the materials to be printed.

Corresponding advantages can be achieved in accordance with examples of certain aspects of the invention by incorporating hydrophilic particles into hydrophilic flowable materials, and hydrophobic particles into hydrophobic flowable materials.

For example, ptfe particles (from BDH Laboratory Chemicals) of about 5 micron in size can be used, as can silica gel particles (same source) about 15 micron in size. The particles can for example be roughly spherical, or they can be porous in themselves. Also usable are for example polystyrene and other polymer latices, either chemically modified or unmodified, preferably uncharged, but possibly charged.

Such particles can usefully be incorporated in:

- (i) Materials to be printed to form membranes, e.g. electroactive membranes, such as chemically selective membranes, e.g. ion-selective membranes to overcoat electrochemical electrodes. Suitable compositions for such membranes include for example compositions based on pvc including ionophore, plasticiser, and optionally solvent.
- (ii) Materials to be printed to form reagent layers, releasable or otherwise, e.g. compositions such as aqueous compositions including salts, oxidants, reductants, enzymes, and/or enzyme substrates, optionally

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including thickeners, (e.g. polyvinyl alcohol or polyvinylpyrrolidone) and/or humectants (e.g. saccharides such as glucose, sucrose, lactose or maltose).

- (iii) Materials to be printed to form structural components of printed devices, e.g. glue tracks or spacer tracks, partitions or barriers.

The particles may include conductive particles, e.g. in connection with materials to form ion-selective membranes.

The invention includes for example applying such materials on printed layers in succession, optionally allowing for intermediate drying and/or curing: e.g. the formation of overlayers, such as for example porous membranes such as cellulose acetate membranes overlying a layer of another material such as an ion-selective membrane or a water-soluble layer capable of releasing its content into contacting aqueous liquid. Such overlayers may be useful to control diffusion or access or exit of materials to or from the underlying layer or device component.

The quantity of particles can be chosen and adjusted to suit the viscosity requirements. For example, 20-40% v/v of ptfe particles 3-15 micron can be used in pvc membrane printing compositions. Lower amounts may be needed of smaller particles, and higher amounts of larger particles. The particles will often be sufficiently dilute in the printing compositions that they are out of direct contact with each other in the resulting dried and/or cured layers, e.g. out of electrical contact where conductive particles are used.

The surfaces to be printed may be flat or curved. The printing process may be a screen-printing process

- involving a mesh and squeegee, or for example a contact (or offset) roller-printing process in which there may be used an apertured mask, or any other suitable printing process for depositing a pattern of detail upon a
- 5 substrate. Particle size is related to size of mesh (where used) so that the particles easily pass through - e.g. particle size may be less than half the mesh aperture size.
- 10 The printing compositions are preferably de-gassed in normal and known manner before use, and if necessary and appropriate the particles disaggregated before use, e.g. by stirring.
- 15 A suitable initial viscosity (i.e. at low shear rates) for the compositions is for example in the range of about 1 to about 250 poise, e.g. at least about 150 poise, and preferably of the order of about 20,000 cps, i.e. 200 poise, when measured in a Brookfield RVT
- 20 viscometer, spindle 6, at 20 rpm, and 25 deg. C.
- It is quite common to find that the viscosity of binders in usual nonaqueous systems is higher than in the aqueous case. It is useful to try and use as high a
- 25 proportion of solids as possible in the (usually) nonaqueous compositions in which the reagents form all or part of the particulate materials, as in that case the particulates comprise the active substances. In the (usually) aqueous systems comprising inert particles we
- 30 try and use as little as possible of the particles which are only inert materials. 10 - 15% w/w or in some cases as low as about 1% has often been found an adequate particle content for the latter systems, while particle contents of up to about 60% can be usable in the former
- 35 systems.

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Preferably the compositions also show appreciable shear-thinning to a viscosity in the range of about 1 to 35 poise at a shear rate of 100 reciprocal seconds, preferably at least about 20 poise, e.g. about 30 poise.

5

In practice it has been found that many suitable examples of the compositions show a shear-thinning at a rate corresponding to a reduction of at least about 0.1 in log viscosity (base 10) per tenfold increase in shear rate within a range of shear rates from about 10 to about 100 reciprocal seconds, and up to 0.6 log viscosity units, preferably in the range 0.3 to 0.6 log viscosity though in certain cases it may not be practicable to formulate for shear-thinning rates as much as these.

15

In practice, it has been found that many of the screen-printing compositions according to the invention are of suitable properties for printing when the directions given herein are followed and they have had a consistency like that of mustard or a mayonnaise sauce.

20

It is sometimes found that uniformity of the dried printed layers can be improved by including a small amount of surfactant in the printing composition, e.g. of the order of about 0.1%, e.g. a neutral tween (trade mark) surfactant.

25

Illustrative embodiments of this invention are given in and by the following examples.

30

#### Example 1

One form of printing composition can be made by the following steps:

- 10 -

(a) dissolve the reagent(s) to be deposited in a chosen solvent, e.g. water or other aqueous solvent such as a buffer suitable for a biochemical reagent to be handled;

5 (b) add a polymer binder, such as for example polyvinylpyrrolidone (pvp), polyvinylalcohol (pva), and/or sodium carboxymethylcellulose (scmc);

(c) add fine inert particle material, e.g. in an amount in the range of about 1 to 15% by weight of the final composition.

10

In each case the ingredients should be thoroughly mixed, e.g. in a ball mill or cavitation mixer.

15 Preferred conditions for making compositions of this form are as follows:

A preferred polymer binder is a mixture of pvp 30% and pva 5% (both on w/v basis as a proportion of the liquid part of the final composition).

20

A preferred type of particles for thickening the composition is silica gel particles of average particle size about 15 microns, 5 to 15%, e.g. 10% by weight of the final composition. An alternative example of

25 particles for thickening purposes is Aerosil 200 from Degussa, average particle size 1/4 micron chain-forming particles, which can be used in quantity such as 1 to 3% by weight.

30 Example 2

A second form of printing composition can be made as follows:

35 (a) take the reagent(s) to be deposited in solid form and comminute them, e.g. by grinding in a ball mill;

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(b) disperse the comminuted reagent particles in a polymer solution.

5 A preferred example formulation of a printing composition of this kind, suitable for printing a reagent mixture essentially comprising glucose oxidase enzyme and potassium ferricyanide for the electrochemical measurement of glucose concentrations is as follows:

10 Grind a mixture of solids consisting of 64% potassium ferricyanide, 32% phosphate buffer salt for pH about 7, and 4% glucose oxidase enzyme, in a ball mill until nearly all the particles, are no more than 10 microns in size. It is often then found that the resulting mixture  
15 of particles are to the extent of about 90% within the size range 1 to 10 micron.

To the ground solids (50 parts by weight) is added first 40 parts by weight of a mixture of cellulose acetate  
20 (thickener/binder) in cyclohexanone (solvent), and then 10 parts by weight of isophorone (slow evaporating solvent, obtainable from Aldrich Chemical Co.). In each case the ingredients should be thoroughly mixed, e.g. with a ball mill or cavitation mixer.

25

### Example 3

Figure 1 of the accompanying drawings shows in diagrammatic cross-sectional scheme an example of an  
30 electrode-containing capillary cell device to illustrate one example of the environment within which reagent layer(s) can be deposited according to an embodiment of the invention. (See also EP 0 225 061.) In Figure 1, at numerals 1 and 2, there are shown opposite walls of the  
35 capillary cell. Other structure is omitted from the diagrammatic drawing apart from electrode(s) and reagent

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layer(s) and a partition which for certain uses will be omitted. Such other structure can include e.g. further circumferential sealing materials, handling pieces, sample intake lip, and intake aperture(s). The capillary gap can conveniently be of the order of 0.1-1 mm.

The capillary cell device is of a size to be handled easily, e.g. about 5cm x 2.5cm. Alternative examples can be smaller, e.g. 2cm x 1cm. The device comprises an upper (e.g. plastics, glass, or ceramic) plate and a lower (e.g. similar) plate (about 1mm thick) fixed together in parallel opposed and spaced relation, less than 1mm apart, by bonding tracks of suitable (e.g. epoxy) adhesive to form a capillary cell cavity, open at one or both ends, which communicates with the outside through a first discontinuity in the bonding arranged to form a cell aperture at one side of the plates. Another discontinuity can be present at the other end of the bonding tracks, to leave another aperture, to allow exit or air when a sample liquid is loaded into the cell. One plate is larger than the other plate and has an end portion extending away from the aperture. This end portion acts as a platform or threshold or lip onto which a droplet of sample liquid can be applied, so that this liquid can be made to fill the capillary cell cavities by capillary flow. The cavity attracts and contains a definite and adequately reproducible volume of liquid when loaded in this way.

Spaced-apart electrodes 3 and 4 are shown as layers fixed to the surface of wall 2 of the cell. Electrodes 3 and 4 can be made according to the intended use of the device: in the present embodiment they are silver-silver halide electrodes (for potentiometry), most preferably silver-silver chloride electrodes, made by applying and drying conductive paint onto the surface of wall 2, the

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conductive paint being a silver-particle-containing  
conductive paint as commercially available and used in  
the fabrication of hybrid electronic circuitry. In  
alternative embodiments for amperometric use the  
5 electrodes can usefully be for example noble-metal  
electrodes e.g. silver or gold, or carbon electrodes.

In the device shown in Figure 1 a membrane barrier 5  
less than 1 mm thick separates the two silver/silver  
10 chloride electrodes: this can be applied as a track of  
material comprising a mixture of pvc, solvent,  
plasticiser and ionophore (e.g., valinomycin in the case  
of a potassium-selective membrane) to one of the plates  
before the second plate is applied to form the capillary  
15 cell. The track of material can be applied for example by  
screen- printing, as can the other layers of materials to  
be deposited. A suitable example composition for the  
track of material is 1% valinomycin, 66% dioctyl sebacate  
and 33% polyvinylchloride dissolved in tetrahydrofuran,  
20 e.g. at a concentration of about 0.08-0.1 gram of the  
mixture per ml of the solvent. Particles can be added to  
improve the printing qualities of the composition, e.g.  
inert particles as detailed below.

25 A releasable layer 6 containing potassium nitrate is  
coated on the wall of the capillary cell opposite one  
electrode. This coating is a releasable coating (e.g. a  
sucrose glaze) to be released into one compartment only  
and to dissolve in the sample liquid to give a standard  
30 concentration of potassium ion when this is taken up into  
the capillary cell.

In a preferred alternative, in place of sucrose,  
polyvinylpyrrolidone, (50% w/v) is used as a carrier base  
35 in which to dissolve the salt which is to form a  
releasable layer. Also, 2% cellulose acetate dissolved



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in cyclohexanone, is preferably sprayed lightly over the releasable coating to form when dry an additional thin surface layer which acts to retard the release of salt when the cell is filled. The salt/pvp layer dries quickly in atmospheric air after screen-printing, and the cellulose acetate is applied after it has dried.

A presently preferred example of materials to prepare an electrochemical analysis cell, according to one embodiment of the invention, is as follows:

A capillary-fill cell is made according to the general form shown in EP 0 225 061, with a preferred composition as follows to be used for the track of material to be screen-printed onto one of its internal surfaces to provide an electroactive barrier:

(a) In the case of a potassium-sensitive cell a screen-printing composition is preferably made as follows:

Mix 44.5g dioctyl phthalate, 5.5g pvc of m.w. 100,000, 12.5g cyclohexanone, together, and heat to dissolve the pvc, to give a solution. To this is added a solution containing : 0.5g valinomycin (in the case of a potassium-sensitive electrode) dissolved in 2.5 ml of tetrahydrofuran, (containing 5 mgm of potassium tetrakis-parachlorophenyl borate) at a temperature below 50 deg C, with stirring. To the mixture is added: 12.5g of 5-micron ptfе particles (from BDH) (slowly while stirring vigorously).

This composition can be used for screen-printing an ion-sensitive membrane.

(b) In the case of a sodium-sensitive cell, the composition is preferably varied as follows: Monensin

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(ionophore for making sodium-sensitive membranes) is used instead of valinomycin in a 1-gram amount, and with proportionately more THF to produce a solution which is then used in place of the valinomycin solution.

5

Among the practicable variations is the use of other kinds of small particles (e.g. about 20% silica gel particles by weight based on the weight of the whole composition, 15 microns in size as obtained from BDH Laboratory Chemicals), optionally together with a thickener such as pvp, as part of the aqueous-based compositions to be used for printing patchwise releasable reagent layers and hydrophilic (e.g. cellulose acetate) membrane layers.

15

#### Example 4

(In this and the following examples, phosphate buffer means a substantially equimolar mixture of potassium hydrogen phosphate and dipotassium hydrogen phosphate, adjusted to give a pH of 7 when at approximately 1M concentration.)

20

A printing composition for screen-printing a layer of reagent material for a cell to measure glucose and sucrose electrochemically (amperometry etc of ferrocyanide produced by action of glucose oxidase on glucose, possibly liberated by invertase) is as follows:

25

Solids: 25.8% potassium ferricyanide, 13.3% phosphate buffer, 1.7% glucose oxidase, 0.8% invertase, and liquids: 41.7% of a solution of ethylcellulose (5%) in cyclohexanone, and 16.7% of a solution of cellulose acetate (10%) in cyclohexanone.

35

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The solids were comminuted together in a ball mill as described elsewhere herein, then suspended in the liquids and screen-printed to give a density of about 3 mg/sq. cm of the dried layer material.

5

The composition of the final coating after drying is:

Potassium ferricyanide - 57.7% phosphate buffer - 28.8%  
glucose oxidase - 3.6% invertase - 1.8%  
10 ethylcellulose - 4.5% cellulose acetate - 3.6%

#### Example 5

15 A printing composition for screen-printing a layer of reagent material for a cell to measure glucose electrochemically is as follows:

Solids: 32.5% potassium ferricyanide, 16.5% phosphate  
buffer, 1% glucose oxidase, and liquid: 50% of a solution  
20 of cellulose acetate (10%) in cyclohexanone.

The solids were comminuted together in a ball mill as described elsewhere herein, then suspended in the liquid and screen-printed to give a density of about 3 mg/sq cm  
25 of the dried layer material.

The composition of the final coating after drying is:

Potassium ferricyanide - 59.1% phosphate buffer - 30%  
30 glucose oxidase - 1.8% cellulose acetate - 9.1%.

#### Example 6

35 A printing composition for screen-printing a layer of reagent material for a cell to include the function of a quinhydrone pH electrode is as follows:

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Solids: 58.8% sodium chloride, quinhydrone 2%, and liquid: 39.2% of a solution of cellulose acetate (10%) in cyclohexanone.

- 5 The solids were comminuted together in a ball mill as described elsewhere herein, then suspended in the liquid and screen-printed to give a density of about 3 mg/sq cm of the dried layer material.
- 10 The composition of the final coating after drying is:
- sodium chloride - 91%; quinhydrone - 3%; cellulose acetate - 6%.
- 15 Variants of the present invention can be applied to facilitate the construction of devices such as those shown in for example EP 0 171 148, 0 170 375, 0 186 286, and 0 225 061, and European Patent Application 87306513.0 (International application GB/87/00526) the disclosures
- 20 of all of which specifications are hereby incorporated by reference.

The several features and characteristics described herein, including those referred to in the claims and

25 illustrated in and by the drawings, are disclosed and can be used in all combinations, subcombinations and variations, as may be desired.

## Claims:-

1. A test device for carrying out a microchemical test, comprising a container for contacting a reaction liquid  
5 during performance of said test, said container having deposited on a surface thereof which in use is to contact said reaction liquid, an adherent layer applied in an amount in the range 1 to 40 mg/sq cm comprising a chemically or electrochemically active material which has  
10 been deposited in the form of a composition comprising solid particles having a particle size in the range 0.5 to 25, e.g. 1 to 20, microns, together with a polymeric binder.
- 15 2. A test device according to claim 1, wherein said particles comprise inert particles, e.g. ptfe or silica gel, and are dispersed in a matrix comprising said active material and a polymeric binder, e.g. a water-soluble cellulose derivative.
- 20 3. A test device according to claim 1, wherein said particles comprise said active material in solid finely-divided form, and are dispersed in a polymeric binder, e.g. a water-soluble cellulose derivative.
- 25 4. A process for manufacturing a test device according to claim 1, comprising printing a layer of a chemically or electrochemically active material on to a surface of a substrate which is to form an inner surface of a  
30 container for carrying out a microchemical test, said process also comprising:
  - (a) providing a printable composition comprising said chemically or electrochemically active material, together  
35 with suspensible hydrophobic or hydrophilic particles having a particle size in the range 0.5 to 25 microns,

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(b) printing said printable composition containing said particles on to said substrate to form a layer on said surface, and

5

(c) causing said layer to dry or solidify.

5. A process according to claim 4, wherein said  
10 chemically or electrochemically active material is water-soluble, e.g. selected from enzymes, antigens, antibodies, electron transfer agents able to react with enzymes, or pH buffer materials.

15 6. A process according to claim 4, wherein the active material is an ion-selective ionophore material.

7. A process according to claim 4, wherein the particle  
20 size is in the range from atleast about 3 micron to at least about 15 micron, and the particles are selected from ptfe, silica-gel, polystyrene, polymer latex, and comminuted solids comprising the chemically or electrochemically active material to be deposited, in an  
25 amount from at least about 1 percent to at least about 60 percent, e.g. about 5 to about 15 percent, by weight of the printable composition.

8. A printable composition for printing a layer of a  
30 chemically or electrochemically active material on to a surface of a substrate to form a device according to claim 1, comprising

(a) a chemically or electrochemically active substance to  
35 be deposited, dissolved in

(b) a (e.g. aqueous) solvent for said substance (a),

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(c) a polymeric binder or thickener dissolved or dispersed in solvent (b),

- 5 (c) from 1 to 15 percent by weight of a dispersed finely-divided inert particulate material with a particle size in the range 1 to 50 microns,

10 said composition having a viscosity in the range 1 to 250 poise at 25 deg.C.

9. A printable composition for printing a layer of a chemically or electrochemically active material on to a surface of a substrate to form a device according to claim 1, comprising

15 (a) a polymeric binder or thickener dissolved or dispersed in a (e.g. nonaqueous) solvent, having dispersed therein

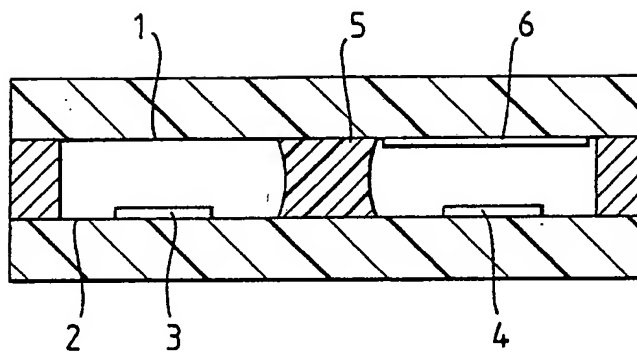
20 (b) from 5 to 60 percent by weight of a chemically or electrochemically active (e.g. water-soluble or water-dispersible) substance to be deposited, in finely-divided solid particulate form having a particle size less than 25 20 micron, preferably less than 10 micron,

30 said composition having a viscosity in the range 1 to 250 poise, preferably at least about 150 poise, at 25 deg.C.

10. A printable composition according to claim 8 or 9, wherein said composition shows shear-thinning of at least about 0.1 log viscosity per tenfold increase of shear rate in the range of shear rates about 10 to 100 reciprocal seconds, and has a viscosity at 200 reciprocal seconds at 25 deg.C. in the range 1 to 35 poise.

//

*Fig.1.*





# INTERNATIONAL SEARCH REPORT

International Application No PCT/GB 87/00770

| <b>I. CLASSIFICATION OF SUBJECT MATTER</b> (if several classification symbols apply, indicate all) <sup>6</sup><br>According to International Patent Classification (IPC) or to both National Classification and IPC<br>IPC <sup>4</sup> : G 01 N 33/52; C 09 D 11/02  |   |                                     |  |  |  |   |   |           |   |    |     |   |   |     |   |  |     |   |  |     |   |   |  |   |  |  |   |  |  |    |  |  |
|--|---|-------------------------------------|--|--|--|---|---|-----------|---|----|-----|---|---|-----|---|--|-----|---|--|-----|---|---|--|---|--|--|---|--|--|----|--|--|
| <b>II. FIELDS SEARCHED</b><br><div style="text-align: center; border-top: 1px solid black; border-bottom: 1px solid black;">Minimum Documentation Searched <sup>7</sup></div> <table style="width: 100%; border-collapse: collapse;"> <tr> <th style="width: 30%; text-align: left; border-bottom: 1px solid black;">Classification System</th> <th style="width: 70%; text-align: left; border-bottom: 1px solid black;">Classification Symbols</th> </tr> <tr> <td style="border-right: 1px solid black; padding: 5px;">IPC<sup>4</sup></td> <td style="padding: 5px;">G 01 N</td> </tr> </table> <div style="text-align: center; border-top: 1px solid black; border-bottom: 1px solid black;">Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched <sup>8</sup></div>   |   |                                     | Classification System  | Classification Symbols   | IPC <sup>4</sup>   | G 01 N  |   |           |   |    |     |   |   |     |   |  |     |   |  |     |   |   |  |   |  |  |   |  |  |    |  |  |
| Classification System  | Classification Symbols  |                                     |  |  |  |   |   |           |   |    |     |   |   |     |   |  |     |   |  |     |   |   |  |   |  |  |   |  |  |    |  |  |
| IPC <sup>4</sup>   | G 01 N  |                                     |  |  |  |   |   |           |   |    |     |   |   |     |   |  |     |   |  |     |   |   |  |   |  |  |   |  |  |    |  |  |
| <b>III. DOCUMENTS CONSIDERED TO BE RELEVANT <sup>9</sup></b> <table style="width: 100%; border-collapse: collapse;"> <tr> <th style="width: 10%; text-align: left; border-bottom: 1px solid black;">Category <sup>9</sup></th> <th style="width: 60%; text-align: left; border-bottom: 1px solid black;">Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup></th> <th style="width: 30%; text-align: left; border-bottom: 1px solid black;">Relevant to Claim No. <sup>13</sup></th> </tr> <tr> <td style="vertical-align: top; border-right: 1px solid black; padding: 5px;">P, X</td> <td style="padding: 5px;">EP, A, 0200539 (EASTMAN KODAK CO.)<br/>5 November 1986, see the whole document</td> <td style="vertical-align: top; padding: 5px;">1-3, 8, 9</td> </tr> <tr> <td style="vertical-align: top; border-right: 1px solid black; padding: 5px;">Y</td> <td style="text-align: center; padding: 5px;">--</td> <td style="vertical-align: top; padding: 5px;">4-7</td> </tr> <tr> <td style="vertical-align: top; border-right: 1px solid black; padding: 5px;">Y</td> <td style="padding: 5px;">US, A, 4216245 (L.C. JOHNSON) 5 August 1980, see the whole document</td> <td style="vertical-align: top; padding: 5px;">1-9</td> </tr> <tr> <td style="vertical-align: top; border-right: 1px solid black; padding: 5px;">Y</td> <td style="padding: 5px;">EP, A, 0016387 (BOEHRINGER MANNHEIM GmbH) 1 October 1980, see the whole document</td> <td style="vertical-align: top; padding: 5px;">1-9</td> </tr> <tr> <td style="vertical-align: top; border-right: 1px solid black; padding: 5px;">Y</td> <td style="padding: 5px;">US, A, 3993451 (B.J. VERBECK) 23 November 1976, see the whole document</td> <td style="vertical-align: top; padding: 5px;">1-9</td> </tr> <tr> <td style="vertical-align: top; border-right: 1px solid black; padding: 5px;">A</td> <td style="padding: 5px;">EP, A, 0115873 (FUJII PHOTO FILM CO., LTD) 15 August 1984</td> <td></td> </tr> <tr> <td style="vertical-align: top; border-right: 1px solid black; padding: 5px;">A</td> <td style="padding: 5px;">EP, A, 0170375 (UNILEVER NV) 5 February 1986<br/>cited in the application</td> <td></td> </tr> <tr> <td style="vertical-align: top; border-right: 1px solid black; padding: 5px;">A</td> <td style="padding: 5px;">EP, A, 0171148 (UNILEVER PLC) 12 February 1986<br/>cited in the application</td> <td></td> </tr> <tr> <td colspan="3" style="text-align: center; padding: 5px;">--</td> </tr> </table> |   |                                     | Category <sup>9</sup>  | Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup>             | Relevant to Claim No. <sup>13</sup>  | P, X  | EP, A, 0200539 (EASTMAN KODAK CO.)<br>5 November 1986, see the whole document | 1-3, 8, 9 | Y | -- | 4-7 | Y | US, A, 4216245 (L.C. JOHNSON) 5 August 1980, see the whole document | 1-9 | Y | EP, A, 0016387 (BOEHRINGER MANNHEIM GmbH) 1 October 1980, see the whole document | 1-9 | Y | US, A, 3993451 (B.J. VERBECK) 23 November 1976, see the whole document | 1-9 | A | EP, A, 0115873 (FUJII PHOTO FILM CO., LTD) 15 August 1984 |  | A | EP, A, 0170375 (UNILEVER NV) 5 February 1986<br>cited in the application |  | A | EP, A, 0171148 (UNILEVER PLC) 12 February 1986<br>cited in the application |  | -- |  |  |
| Category <sup>9</sup>  | Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup>                | Relevant to Claim No. <sup>13</sup> |  |  |  |   |   |           |   |    |     |   |   |     |   |  |     |   |  |     |   |   |  |   |  |  |   |  |  |    |  |  |
| P, X   | EP, A, 0200539 (EASTMAN KODAK CO.)<br>5 November 1986, see the whole document   | 1-3, 8, 9                           |  |  |  |   |   |           |   |    |     |   |   |     |   |  |     |   |  |     |   |   |  |   |  |  |   |  |  |    |  |  |
| Y  | --  | 4-7                                 |  |  |  |   |   |           |   |    |     |   |   |     |   |  |     |   |  |     |   |   |  |   |  |  |   |  |  |    |  |  |
| Y  | US, A, 4216245 (L.C. JOHNSON) 5 August 1980, see the whole document   | 1-9                                 |  |  |  |   |   |           |   |    |     |   |   |     |   |  |     |   |  |     |   |   |  |   |  |  |   |  |  |    |  |  |
| Y  | EP, A, 0016387 (BOEHRINGER MANNHEIM GmbH) 1 October 1980, see the whole document  | 1-9                                 |  |  |  |   |   |           |   |    |     |   |   |     |   |  |     |   |  |     |   |   |  |   |  |  |   |  |  |    |  |  |
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| A  | EP, A, 0170375 (UNILEVER NV) 5 February 1986<br>cited in the application  |                                     |  |  |  |   |   |           |   |    |     |   |   |     |   |  |     |   |  |     |   |   |  |   |  |  |   |  |  |    |  |  |
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| --   |   |                                     |  |  |  |   |   |           |   |    |     |   |   |     |   |  |     |   |  |     |   |   |  |   |  |  |   |  |  |    |  |  |
| <div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p><sup>10</sup> * Special categories of cited documents: <sup>10</sup></p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"Z" document member of the same patent family</p> </div> </div>   |   |                                     |  |  |  |   |   |           |   |    |     |   |   |     |   |  |     |   |  |     |   |   |  |   |  |  |   |  |  |    |  |  |
| <b>IV. CERTIFICATION</b> <table style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 50%; border-right: 1px solid black; padding: 5px;">           Date of the Actual Completion of the International Search<br/>           22nd January 1988         </td> <td style="width: 50%; padding: 5px;">           Date of Mailing of this International Search Report<br/> <div style="text-align: right; font-size: 1.2em;">15 MAR 1988</div> </td> </tr> <tr> <td style="border-right: 1px solid black; padding: 5px;">           International Searching Authority<br/> <div style="text-align: center;">EUROPEAN PATENT OFFICE</div> </td> <td style="padding: 5px;">           Signature of Authorized Officer<br/> <div style="text-align: center;"> <br/>             P.C.G. VAN DER PUTTEN           </div> </td> </tr> </table>   |   |                                     | Date of the Actual Completion of the International Search<br>22nd January 1988 | Date of Mailing of this International Search Report<br><div style="text-align: right; font-size: 1.2em;">15 MAR 1988</div> | International Searching Authority<br><div style="text-align: center;">EUROPEAN PATENT OFFICE</div> | Signature of Authorized Officer<br><div style="text-align: center;"> <br/>             P.C.G. VAN DER PUTTEN           </div> |   |           |   |    |     |   |   |     |   |  |     |   |  |     |   |   |  |   |  |  |   |  |  |    |  |  |
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| International Searching Authority<br><div style="text-align: center;">EUROPEAN PATENT OFFICE</div>   | Signature of Authorized Officer<br><div style="text-align: center;"> <br/>             P.C.G. VAN DER PUTTEN           </div> |                                     |  |  |  |   |   |           |   |    |     |   |   |     |   |  |     |   |  |     |   |   |  |   |  |  |   |  |  |    |  |  |

International Application No. PCT/GB 87/00770

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**ANNEX TO THE INTERNATIONAL SEARCH REPORT  
ON INTERNATIONAL PATENT APPLICATION NO.**

GB 8700770

SA 19197

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